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Photophysics of 6-methoxyquinoline in Nafion® polymer matrix

M S Mehata* and H B Tripathi

Photophysics Laboratory, Department of Physics,
DSB Campus, Kumaon University, Nainital-263 002, India

E-mail : kumaonuniversity@vsnl.com

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Abstract Fluorescence characteristics of 6-methoxyquinoline (6MQ) in Nafion® polymer have been reported. The spectral features as well as transient studies show a similarity for 6MQ in fluid media at low temperatures and in Nafion® matrix at ambient temperature. Excitation wavelength dependence of the fluorescence alongwith the decay measurements across the emission profile show the presence of various conformers in the form of monocations that assume different geometries in the polymer matrix and these conformers undergo excited state charge transfer process.

Keywords : 6-Methoxyquinoline, Nafion®, EERS

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The fluorescence of 6-methoxyquinoline (6MQ) in various polar solvent has been found to exhibit edge excitation red shift (EERS) i.e. a shift of the emission peak when excitation is done towards the red edge of the first absorption band, which is interpreted as being due to solvent reorientation relaxation in the excited state [1-2]. Various effects (viscosity, the solvent and its concentration) have been reported earlier by Itoh and Azumi [3]. Ikeyama *et al.* [4] have shown that in the fluorescence spectrum of 6MQ in ethanol at 294K, a time-dependent spectral shift is observed when the solvent relaxation time (τ_r) is of the order of fluorescence lifetime.

Schulman *et al.* [5] have studied the photochemistry of 6MQ as a function of pH and have shown that at a pH<4, only the emission of the monocation ($6MQ^+$) with emission maximum around 445 nm is observed, whereas absorption maximum of L_a and L_b bands are at 313 nm and 337 nm respectively. From a pH of 4 to 6, the fluorescence of the cation falls and the fluorescence of the neutral species appears to finally rise to its maximum value at a pH of 12. In aqueous solution (pH = 7), it was suggested that 6MQ undergoes proton transfer reaction in excited state [2] due to an increased basicity of 6MQ on excitation. For an intermediate pH of 6 to 10, the fluorescence of the cation and the neutral molecule remain constant.

* Corresponding Author.
E-mail : msmehata@yahoo.com

From the temperature dependence of the fluorescence characteristics, it was suggested that at 160K, a rapid charge transfer (CT) from the methoxy group to the quinoline ring takes place followed by a solvent reorientation relaxation at ambient temperature [6]. It has been reported recently [7, 8] that the probe molecule (6MQ) may be used as a chloride ion sensor as well as a probe molecule for the solvation dynamics studies.

In rigid media, however, the dynamic equilibrium between the different solvation sites is lost, and an emission will occur from a Franck-Condon excited state corresponding to the solvation site specifically excited [9]. The relaxation rate constant of different solvation sites are different and smaller than the fluorescence rate constant. This leads to excitation wavelength dependence of the fluorescence and hence the observation of red edge effect (REE) in the emission spectra in rigid media [10]. The second kind of red edge excitation effect is observed for flexible molecules like the ter-butyl ester of 9-anthroic acid (9TBA) and tetra phenyl butadiene (TPB) in rigid matrices [11], and is due to the different conformers of varying geometries which absorb different energies. In fluid media, these conformers interchange rapidly ; however, in rigid media, the molecules are trapped in certain geometric configurations. This depends upon the nature (viscosity, free volume and the polarity) of the polymer matrix [12].

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In the present paper, we report the fluorescence characteristics of 6MQ in a Nafion® film. The polymer reacts as a cation (ion) exchanger [13] having a polar head group SO_3H^+ and is highly acidic in nature. The structure of $6MQ^+$ monocation and Nafion® are given in Figures 1 and 2 respectively.

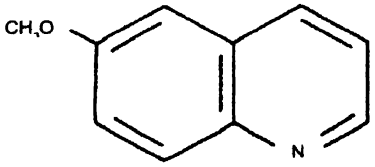

Figure 1. Chemical structure of 6-methoxyquinoline monocation ($6MQ^+$).

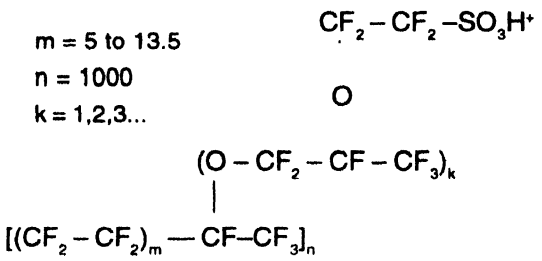

Figure 2. Chemical structure of Nafion®

6-Methoxyquinoline (Aldrich Chemical, USA) is used and is checked for its purity. Nafion® – 117 film (Aldrich) was cleaned by first boiling in nitric acid and then in distilled water for about half an hour. 6MQ was separately loaded in the Nafion® film from aqueous solution. The estimated concentration for these measurements was about 10^{-5} M.

The absorption, fluorescence and excitation spectra were recorded with Jasco V-550 spectrophotometer and Jasco FP-777 spectrofluorometer respectively. Fluorescence decay was measured with Edinburgh Instrument-199 time domain spectrometer using the time-correlated single-photon counting technique. The decay analysis is done by available FLA-900 software. The goodness of fit is judged by the residuals and their χ^2 - value.

Figure 3 shows an absorption and peak normalized excitation spectra of 6-methoxyquinoline in Nafion® film. The low energy absorption band L_b (341 nm) in this matrix is slightly red shifted as compared to the band in solution (337 nm). However, the band at 313 nm (L_a) remains same. The excitation spectrum is red shifted with respect to the absorption spectrum and also exhibit successive red shifts corresponding to longer wavelengths of the emission profile.

Figure 4 shows some peak-normalized fluorescence spectra for different excitation wavelengths of 6MQ in Nafion® film. A red shift from 431 to 448 nm (~ 880 cm^{-1}) is observed in the emission maximum when the excitation wavelength is increased from 350 to 400 nm (red edge of the first absorption band). The shape and the full width at half maximum (FWHM) of the emission

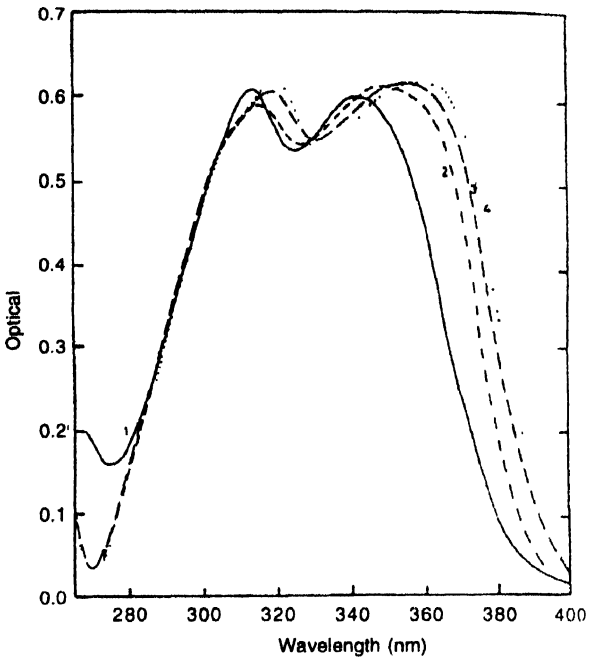

Figure 3. Absorption spectrum (1) and excitation spectra of 6MQ in Nafion® film for λ_{em} = 400 nm (2), λ_{em} = 430 nm (3) and λ_{em} = 475 nm (4).

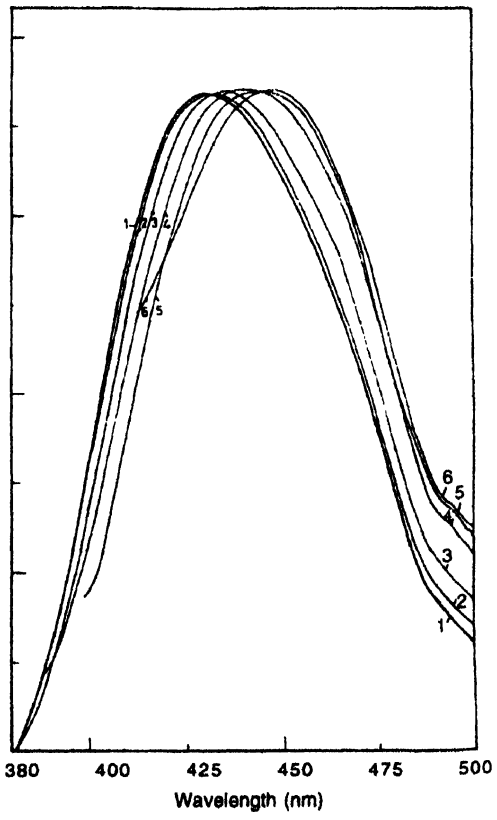

Figure 4. Excitation wavelength dependence of some peak-normalized emission spectra of 6MQ in Nafion® film at 296K for λ_{ex} = 350 nm (1), λ_{ex} = 360 nm (2), λ_{ex} = 370 nm (3), λ_{ex} = 380 nm (4), λ_{ex} = 390 nm (5) and λ_{ex} = 400 nm (6).

spectra remain the same throughout the range of excitation wavelength (*i.e.* 350-400 nm).

The observed spectra (absorption and emission) with the polymer matrix resemble the solution spectra for a pH of 2, and the slight shift in band position may be due to the high viscosity of the Nafion® matrix relative to solution phase. The spectral features indicate the presence of monocation species ($6MQ^+$) [1 o] in Nafion® matrix.

The observed behaviour can be explained in the following manner. In Nafion® polymer matrix, the 6MQ monocation forms different geometric conformers. Each conformer has its own emission spectrum. All the conformers of $6MQ^+$ monocation at room temperature shows emission from locally excited state (LE) as well as charge transfer state (CT). However, depending on the geometry, the emitting state is different for different conformers. On excitation by red edge of the absorption band, only those molecules are excited which have proper configuration corresponding to the excitation energy and hence the emission for those conformers will be red shifted relative to the emission for short wavelength excitation. Similarity of the shape and the FWHM of the emission spectra for short and long wavelength excitations, shows that the de-excitation pathways are similar for all the conformers although the rate may be different.

The lifetime data of 6MQ in Nafion® film are given in Table 1. From the table it may be seen that the decay data fit with a double exponential function throughout the emission profiles. A single exponential decay function fails to describe the observed decay as evidenced by the larger χ^2-value, large non-random residuals and a consequently large standard deviation (Figure 5). Throughout the emission wavelengths probed, the decay follows the function

$$I(\lambda,t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right),$$

where $I(\lambda)$ is the intensity at the emission wavelength λ, τ_1 and τ_2 are the two fluorescence lifetimes and α_1 and α_2 are the decay-associated parameters respectively. It may be noted that the fluorescence lifetimes τ_1 and τ_2 both increase when the decay curves are collected at longer emission wavelengths. The amplitude α_1 corresponding to τ_1 decreases while α_2 increases with increasing emission wavelength.

Table 1. Lifetime parameters of 6MQ in Nafion® matrix at 296K (λ_{ex} = 360 nm).

λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	α_1	α_2	χ^2
390	6.59 (0.17)	18.37 (0.13)	43.72	56.28	1.07
410	8.25 (0.13)	21.99 (0.22)	42.66	57.40	1.09
430	9.58 (0.18)	24.58 (0.27)	42.10	57.90	1.08
450	10.53 (0.18)	26.41 (0.26)	39.61	60.39	1.10
470	10.69 (0.19)	26.94 (0.25)	38.15	61.85	1.13
500	10.78 (0.21)	27.41 (0.24)	34.33	65.67	1.12

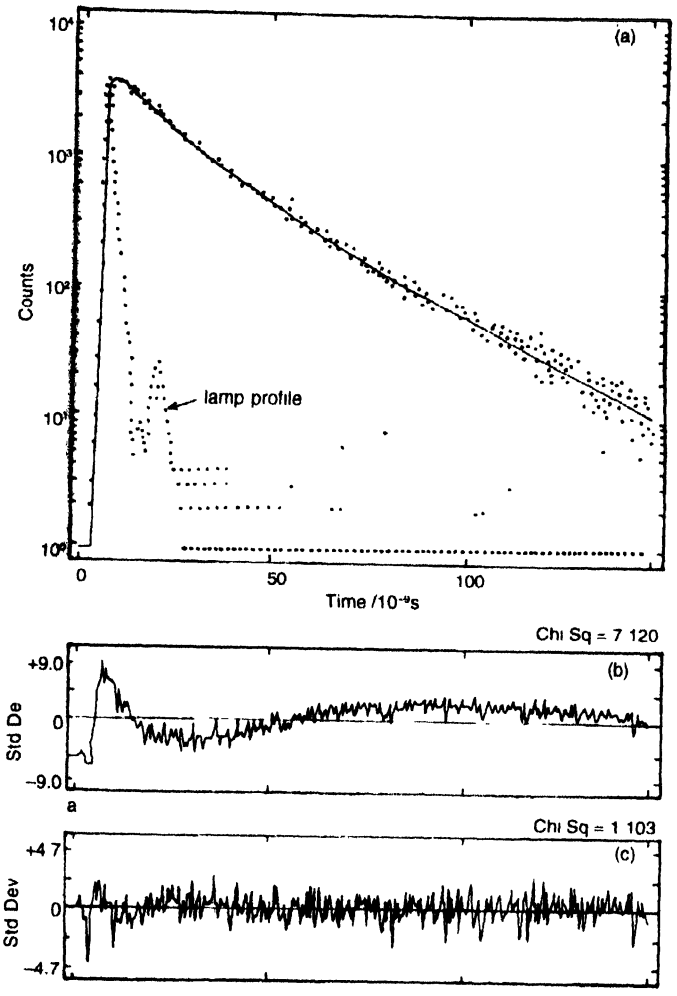

Figure 5. (a) Two component fit with two fluorescence lifetimes for the fluorescence decay of 6MQ in Nafion® film at λ_{ex} = 360 nm, λ_{em} = 450 nm. The residuals and the χ^2-values are for (b) the single exponential fit and (c) the two exponential fit.

The result (EERS) can be explained, with the help of a broad distribution function model similar to 4-dimethylaminobenzonitrile (DMABN) [14], representing various conformers, which are not inter-convertible during the lifetime of the solute. Therefore the multi-exponential decay can be understood in terms of activated processes due to various trapped geometries of the molecules. In a broad distribution model, the multi-component decay curve can be fitted with two or three component (exponential) model. It is interesting to note that the decay parameters for 6MQ in Nafion® matrix at room temperature have a close resemblance with the data for 6MQ in $1NH_2SO_4$ (glycerol : water) at 160K [6]. Similar to glassy media, the two decay components for 6MQ in Nafion® result from the normal species and charge transfer species. However, the increase in the decay time across the emission profile may be due to different geometries of the solute. The molecules trapped in different geometries have different fluorescence lifetimes for normal and charge transfer emissions.

From above study, it is apparent that in the polymer Nafion® matrix, 6MQ exhibit emission due to monocation which are in different geometric configurations and exhibit Red Edge Effect (REE) in emission. The conformers on excitation undergo a slow charge transfer from methoxy group to quinoline ring (activated processes) and thus the emission shows a biexponential decay corresponding to the normal and the charge transferred species. However, different conformations have different lifetimes for normal and charge transfer emissions as exhibited by an increase of lifetime across the emission profile.

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References

[1] D Pant, H B Tripathi and D D Pant *J. Photochem Photobiol A : Chem* **56** 207 (1991)

[2] D Pant, H B Tripathi and D D Pant *J. Lumin* **51** 223 (1992)

[3] K Itoh and T Azumi *J. Chem. Phys* **62** 3431 (1975)

[4] T Ikeyama, T Azumi, T Murao and I Yamazaki *Chem Phys Lett* **96** 419 (1983)

[5] S G Schulman, R M Threatte, A C Campomacchia and W L Poul *J. Pharm Sci.* **63** 876 (1974)

[6] D Pant, H B Tripathi and D D Pant *J. Photochem Photobiol A : Chem.* **54** 239 (1990)

[7] M S Mehata and H B Tripathi *Anal. Lett* (communicated)

[8] A Martin and R Narayanaswamy *Sensors and Actuators* **B38-39** 330 (1997)

[9] K A Al-Hassan *J. Polym. Sci.* **B26** 1727 (1988)

[10] K A Al-Hassan and M A El-Bayoumi *J. Polym Sci* **25** 195 (1987)

[11] K A Al-Hassan, M A El-Bayoumi *Chem. Phys Lett* **123** 93 (1986)

[12] H C Joshi, A Upadhyay, H Mishra, H B Tripathi, D D Pant *J. Photochem Photobiol A : Chem* **122** 185 (1999)

[13] O J Rolinski and D J S Birch *Meas Sci Technol* **10** 127 (1999)

[14] K A Al-Hassan and T Azumi *Chem Phys. Lett* **163** 129 (1989)